



PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

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Wataru OGUCHI, et al.

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Group Art Unit: 1625

Confirmation No.: 2068

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For: CRYSTALLINE MWW-TYPE TITANOSILICATE CATALYST FOR PRODUCING OXIDIZED COMPOUND, PRODUCTION PROCESS FOR THE CATALYST, AND PROCESS FOR PRODUCING OXIDIZED COMPOUND BY USING THE CATALYST

SUBMISSION OF VERIFIED ENGLISH LANGUAGE TRANSLATION

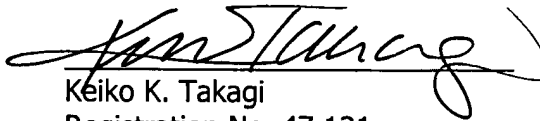
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Applicants respectfully submit herewith the Verified English Language Translation (sixty-nine (69) pages of specification plus executed translator's Declaration) for provisional application no. 60/247,963 filed in the Japanese language.

Respectfully submitted,

SUGHRUE MION, PLLC
Telephone: (202) 293-7060
Facsimile: (202) 293-7860


Keiko K. Takagi
Registration No. 47,121

WASHINGTON OFFICE

23373

CUSTOMER NUMBER

Date: March 5, 2004




DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/247,963 filed on November 14, 2000.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 26th day of May, 2001


Atsuko Ikeda

[NAME OF DOCUMENT] Specification

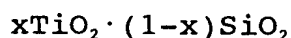
[TITLE OF THE INVENTION]

Crystalline MWW-Type Titanosilicate Catalyst for
Production of Oxidized Compound, Production Process
for the Catalyst, and Process for Producing Oxidized
Compound Using the Catalyst

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound, which is a catalyst for use in producing an oxidized compound by an oxidation reaction of a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or more other functional group using a peroxide as an oxidizing agent, wherein said catalyst has an MWW structure and is represented by the following composition formula (1):

Composition formula (1)



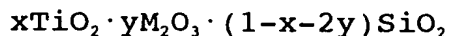
(wherein x is a number of 0.0001 to 0.2).

[Claim 2] The crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in claim 1, wherein x is a number of 0.005 to 0.2.

[Claim 3] A crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound, which is a catalyst for use in producing an oxidized compound by an oxidation reaction of a carbon-carbon double bond of a

compound having a carbon-carbon double bond and one or more other functional group using a peroxide as an oxidizing agent, wherein said catalyst has an MWW structure and is represented by the following composition formula (2):

Composition formula (2)



(wherein M represents at least one element selected from the group consisting of aluminum, boron, chromium, gallium and iron, x is a number of 0.0001 to 0.2 and y is a number of 0.0001 to 0.1).

[Claim 4] The crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in claim 3, wherein M in composition formula (2) is boron.

[Claim 5] The crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in claim 3 or 4, wherein x is a number of 0.005 to 0.2.

[Claim 6] The crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in any one of claims 3 to 5, wherein y is a number of 0.0001 to 0.05.

[Claim 7] A process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound described in any one of claims 1 to 6,

said production process comprising the following first and second steps:

First step:

a step of heating a mixture containing a template compound, a titanium-containing compound, a boron-containing compound, a silicon-containing compound and water to obtain a precursor;

Second step:

a step of calcining the precursor obtained in the first step to obtain a crystalline titanosilicate.

[Claim 8] The process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in claim 7, wherein the template compound is a nitrogen-containing compound.

[Claim 9] The process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in claim 8, wherein the nitrogen-containing compound is at least one compound selected from the group consisting of piperidine, hexamethyleneimine and a mixture thereof.

[Claim 10] The process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in any one of claims 7 to 9, wherein the titanium-containing compound is at least one compound selected from the group consisting of titanium

oxide, titanium halide and tetraalkylorthotitanates.

[Claim 11] The process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in any one of claims 7 to 10, wherein the boron-containing compound is at least one compound selected from the group consisting of boric acid, borate, boron oxide, boron halide and trialkylborons.

[Claim 12] The process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in any one of claims 7 to 11, wherein the silicon-containing compound is at least one compound selected from the group consisting of silicic acid, silicate, silicon oxide, silicon halide, fumed silicas, tetraalkylorthosilicates and colloidal silica.

[Claim 13] The process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in any one of claims 7 to 12, wherein the ratio of titanium and silicon in the mixture of the first step is 0.001 to 0.3 : 1 (titanium : silicon) in terms of the molar ratio.

[Claim 14] The process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in any one of claims 7 to 13, wherein the ratio of boron and silicon in the mixture of the first step is 0.3 to 10 : 1 (boron : silicon) in terms

of the molar ratio.

[Claim 15] The process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in any one of claims 7 to 14, wherein the ratio of water and silicon in the mixture of the first step is 5 to 200 : 1 (water : silicon) in terms of the molar ratio.

[Claim 16] The process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in any one of claims 7 to 15, wherein the ratio of the template compound and silicon in the mixture of the first step is 0.1 to 5 : 1 (template compound : silicon) in terms of the molar ratio.

[Claim 17] The process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in any one of claims 7 to 16, wherein the heating temperature in the first step is in the range of 110 to 200°C.

[Claim 18] The process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound as claimed in any one of claims 7 to 17, wherein the calcining temperature in the second step is in the range of 200 to 700°C.

[Claim 19] The process for producing a crystalline MWW-type titanosilicate catalyst for the production of an

oxidized compound as claimed in any one of claims 7 to 18, wherein the second step is performed after contacting an acid with the precursor obtained in the first step.

[Claim 20] A process for producing an oxidized compound, comprising performing an oxidation reaction of a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or more other functional group using a peroxide as an oxidizing agent in the presence of the crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound described in any one of claims 1 to 6.

[Claim 21] The process for producing an oxidized compound as claimed in claim 20, wherein the oxidizing agent is at least one compound selected from the group consisting of a hydrogen peroxide, a tert-butyl hydroperoxide, a tert-amino hydroperoxide, a cumene hydroperoxide, an ethylbenzene hydroperoxide, a cyclohexyl hydroperoxide, a methylcyclohexyl hydroperoxide, a tetraphosphoric hydroperoxide, an isobutylbenzene hydroxide, an ethylnaphthalene hydroperoxide and a peracetic acid.

[Claim 22] The process for producing an oxidized compound as claimed in any one of claim 20 or 21, wherein the other functional group in the compound having a carbon-carbon double bond and one or more other functional group is at least one functional group selected from the group

consisting of an alkenyl group, an alkynyl group, an aryl group, an arene group, an alcohol group, a phenol group, an ether group, an epoxide group, a halogen group, an aldehyde group, a ketone group, a carbonyl group, an ester group, an amide group, a cyanate group, an isocyanate group, a thiocyanate group, an amine group, a diazo group, a nitro group, a nitrile group, a nitroso group, a sulfide group, a sulfoxide group, a sulfone group, a thiol group, an orthoester group, a urea group and an imine group.

[Claim 23] The process for producing an oxidized compound as claimed in any one of claims 20 to 22, wherein the compound having a carbon-carbon double bond and one or more other functional group is at least one compound selected from the group consisting of allyl ethers, compounds having from 3 to 10 carbon atoms, ethers of polyhydric alcohol, and carboxylic acid esters.

[Claim 24] The process for producing an oxidized compound as claimed in claim 23, wherein the allyl ether is at least one compound selected from the group consisting of an allyl methyl ether, an allyl ethyl ether, an allyl propyl ether, an allyl butyl ether, an allyl vinyl ether and a diallyl ether.

[Claim 25] The process for producing an oxidized compound as claimed in claim 23, wherein the compound having a carbon-carbon double bond and one or more other

functional group is a diallyl ether or an allyl alcohol and the oxidizing agent is hydrogen peroxide.

[Claim 26] The process for producing an oxidized compound as claimed in claim 23, wherein the compound having from 3 to 10 carbon atoms is at least one compound selected from the group consisting of an allyl alcohol, an allyl bromide, an allyl chloride, an acrolein, a methacrolein and an acrylic acid.

[Claim 27] The process for producing an oxidized compound as claimed in claim 23, wherein the ether of polyhydric alcohol is at least one compound selected from the group consisting of an ethylene glycol monoalkenyl ether, an ethylene glycol dialkenyl ether, a 1,2-propanediol monoalkenyl ether, a 1,2-propanediol dialkenyl ether, a 1,3-propanediol monoalkenyl ether, a 1,3-propanediol dialkenyl ether, a 1,2-butanediol monoalkenyl ether, a 1,2-butanediol dialkenyl ether, a 1,3-butanediol monoalkenyl ether, a 1,3-butanediol dialkenyl ether, a 1,4-butanediol monoalkenyl ether, a 1,4-butanediol dialkenyl ether, a pentaerythritol monoalkenyl ether, a pentaerythritol dialkenyl ether, a pentaerythritol trialkenyl ether and a pentaerythritol tetraalkenyl ether.

[Claim 28] The process for producing an oxidized compound as claimed in claim 23, wherein the carboxylic acid ester is at least one compound selected from the group

consisting of an allyl formate, an allyl acetate, an allyl propionate, an allyl tartrate and an allyl methacrylate.

[Claim 29] The process for producing an oxidized compound as claimed in any one of claims 20 to 28, wherein the oxidation reaction is performed in the presence of at least one solvent selected from the group consisting of alcohols, ketones, nitriles and water.

[Claim 30] The process for producing an oxidized compound as claimed in any one of claims 20 to 29, wherein the oxidized compound is a compound resultant from epoxidization of the carbon-carbon double bond site of the raw material compound having a carbon-carbon double bond and one or more other functional group, a compound resultant from diolation of the carbon-carbon double bond site of the raw material compound having a carbon-carbon double bond and one or more other functional group, and/or a mixture thereof.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a crystalline titanasilicate catalyst having a structural code MWW used for a catalyst in an oxidation reaction of a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or more other functional group and also

relates to a process for producing the catalyst and a process for producing an oxidized compound using the catalyst.

[0002]

More specifically, the present invention relates to a crystalline titanosilicate catalyst having a structural code MWW, which can be used as a catalyst in an oxidation reaction of a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or more other functional group using a peroxide as an oxidizing agent; a process for producing the catalyst; and a process for producing an oxidized compound, particularly an epoxy compound, comprising performing an oxidation reaction of a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or more other functional group in the presence of the catalyst.

[0003]

[Background Art]

In general, "zeolite" is long a generic term for crystalline and porous aluminosilicates, and the basic unit of the structure is $(\text{SiO}_4)^{4-}$ or $(\text{AlO}_4)^{5-}$ having a tetrahedral structure. However, it has been recently clarified that a structure peculiar or analogous to zeolite exists in many other oxides such as aluminophosphate.

[0004]

According to the International Zeolite Association (hereinafter simply referred to as "IZA") who defines the zeolite in W. Meier, D.H. Meier, D.H. Olxon and Ch. Baerlocher, Atlas of Zeolite Structure Types, 4th Edition, Elsevier (1996) (hereinafter simply referred to as "Atlas"), substances having the same structure other than aluminosilicate are described as an object substance in prescribing the structure and these are called as a "zeolite-like material".

[0005]

The prehistory to reach this definition is described in detail in Yoshio Ono and Takeaki Yajima, Zeolite no Kagaku to Kogaku (Science and Engineering of Zeolite), Kodansha (July 10, 2000).

[0006]

In the present specification, the definition of "zeolite" follows the definition described in Yoshio Ono and Takeaki Yajima, Zeolite no Kagaku to Kogaku (Science and Engineering of Zeolite), Kodansha (July 10, 2000), where zeolite includes not only aluminosilicates but also substances having an analogous structure such as titanosilicate.

[0007]

In the present specification, the structures of

zeolite and zeolite-like materials are denoted by a structural code using 3 alphabetic capital letters originated in the standard substance first used for the clarification of the structure approved by IZA. The structural code includes those contained in Atlas and those approved after the 4th edition.

[0008]

In the present specification, "aluminosilicate" and "titanosilicate" are not limited at all on the properties such as crystalline or amorphous, or porous or not porous, and unless otherwise indicated, these denote "aluminosilicates" and "titanosilicates" of all properties.

[0009]

In the present specification, the "molecular sieve" means an activity or operation of classifying the molecules by the size and also means a substance having such a function. Zeolite is also included in this molecular sieve. The details thereon are described in Hyojun Kagaku Yogo Jiten (Standard Chemical Glossary), Japan Chemical Association (compiler), Maruzen (March 30, 1991).

[0010]

In recent years, various studies have been made on the oxidation reaction of an organic compound using titanosilicate which is one of zeolites, as a catalyst and using a peroxide as an oxidizing agent. Among these, TS-1

which is one of crystalline titanosilicates has been found to show an activity in an oxidation reaction using various peroxides after the synthetic method thereof was disclosed in U.S. Patent 4,410,501, and has been applied to various reactions. Specific examples thereof include the method disclosed in JP-B-4-5028 (the term "JP-B" as used herein means an "examined Japanese patent publication"), where TS-1 is used as a catalyst in the epoxidization of an olefin compound using a hydrogen peroxide or an organic peroxide as an oxidizing agent.

[0011]

The structural code of TS-1 is MFI, which is the same as the structural code of a representative synthetic zeolite ZSM-5, and contains an oxygen 10-membered ring. Since TS-1 has a relatively small pore size of 0.51 to 0.56 nm as calculated, an epoxidizable olefin compound is limited and moreover, the rate of an olefin compound as a reaction starting material diffusing into the inside of a pore and the rate of an epoxy compound as a reaction product flowing out from the pore are low, so that a reaction activity highly enough for the industrial use cannot be achieved in many cases. Furthermore, a ring opening reaction of the epoxy group of an epoxy compound as a reaction product takes place and the selectivity disadvantageously decreases.

[0012]

On the other hand, JP-A-7-242649 (the term "JP-A" as used herein an "unexamined published Japanese patent application") discloses a method of performing an epoxidization reaction of an olefin compound using a crystalline titanium-containing molecular sieve having a structure similar to aluminum-free zeolite Beta (structural code: *BEA) as a catalyst and using a hydrogen peroxide or an organic peroxide as an oxidizing agent.

[0013]

Since *BEA has a large pore diameter as compared with the structural code MFI of TS-1, an effect of enabling a reaction of a sterically bulky compound or elevating the diffusion rate to improve the reaction rate is expected. In some examples of the above-described patent publication, a compound which does not react by the use of TS-1 can be actually oxidized, however, there are problems that the conversion of an oxidizing agent is low when a hydrogen peroxide is used as an oxidizing agent for the epoxidization reaction and that a ring opening reaction of epoxide takes place to generate a glycol, as a result, the selectivity decreases. Furthermore, in the case of the molecular sieve described in this patent publication, the activity decreases at a high rate, that is, the catalyst life is short, so that a regeneration treatment must be

repeated on great occasions and this is the point disturbing the implementation in an industrial scale.

[0014]

In recent years, synthetic zeolites having a structural code MWW different from MFI or *BEA are attracting an attention. The production process thereof is disclosed, for example, in JP-A-63-297210.

[0015]

Furthermore, according to Peng Wu, Takashi Tatsumi and Takayuki Komatsu, Chemistry Letters, 774 (2000), it has been reported that when a crystalline titanosilicate having the structural code MWW and containing a titanium atom in the crystal structure is produced and then a cyclohexene is oxidized using this as a catalyst and using a hydrogen peroxide, a cyclohexene oxide can be produced.

[0016]

However, the yield of the objective substance is not so high, both epoxide and diol are generated in a fairly large amount, a tendency of selectively giving a certain compound is not seen and therefore, this method has a problem in its industrial use.

[0017]

As described above, various proposals have been made for the oxidation reaction of an olefin compound using a titanosilicate as a catalyst and using a peroxide as an

oxidizing agent, however, industrially practicable techniques are limited and moreover, in any case, only an oxidation reaction of a compound having a simple carbon-carbon double bond is disclosed. There has been not known any case reporting on a titanosilicate which can be used as a catalyst in an oxidation reaction of a compound having a carbon-carbon double bond and one or more other functional group.

[0018]

[Problems to be Solved by the Invention]

The object of the present invention is to provide a crystalline titanosilicate catalyst which can be used as a catalyst in a selective oxidation reaction of a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or more other functional group. The object of the present invention includes providing a process for producing the catalyst and a process for producing an oxidized compound by an oxidation reaction using the catalyst.

[0019]

[Means to Solve the Problems]

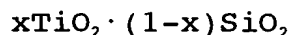
As a result of extensive investigations to solve the above-described problems, the present inventors have found that in a reaction of oxidizing a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or

more other functional group by a peroxide, a crystalline titanasilicate catalyst having a structural code MWW effectively works as a catalyst and highly selectively yields an objective oxidized compound. The present invention has been accomplished based on this finding.

[0020]

More specifically, the present invention (I) is a crystalline MWW-type titanasilicate catalyst for the production of an oxidized compound, which is a catalyst for use in producing an oxidized compound by an oxidation reaction of a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or more other functional group using a peroxide as an oxidizing agent, wherein the catalyst has an MWW structure and is represented by the following composition formula (1):

Composition formula (1)



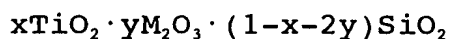
(wherein x is a number of 0.0001 to 0.2).

[0021]

The present invention (II) is a crystalline MWW-type titanasilicate catalyst for the production of an oxidation compound, which is a catalyst for use in producing an oxidized compound by an oxidation reaction of a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or more other functional group using a

peroxide as an oxidizing agent, wherein the catalyst has an MWW structure and is represented by the following composition formula (2):

Composition formula (2)



(wherein M represents at least one element selected from the group consisting of aluminum, boron, chromium, gallium and iron, x is a number of 0.0001 to 0.2 and y is a number of 0.0001 to 0.1).

[0022]

The present invention (III) is a process for producing the crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound of the present invention (I) or (II).

[0023]

The present invention (IV) is a process for producing an oxidized compound, comprising performing an oxidation reaction of a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or more other functional group using a peroxide as an oxidizing agent in the presence of the crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound of the present invention (I) or (II).

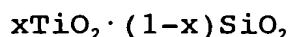
[0024]

[Mode for Carrying Out the Invention]

The present invention is described in detail below.

At first, the present invention (I) and the present invention (II) are described. The present invention (I) is a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound, which is a catalyst for use in producing an oxidized compound by an oxidation reaction of a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or more other functional group using a peroxide as an oxidizing agent, wherein the catalyst has an MWW structure and is represented by the following composition formula (1):

Composition formula (1)



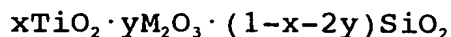
(wherein x is a number of 0.0001 to 0.2).

[0025]

The present invention (II) is a crystalline MWW-type titanosilicate catalyst for the production of an oxidation compound, which is a catalyst for use in producing an oxidized compound by an oxidation reaction of a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or more other functional group using a peroxide as an oxidizing agent, wherein the catalyst has an MWW structure and is represented by the following

composition formula (2):

Composition formula (2)



(wherein M represents at least element selected from the group consisting of aluminum, boron, chromium, gallium and iron, x is a number of 0.0001 to 0.2 and y is a number of 0.0001 to 0.1).

[0026]

In the crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound of the present invention (I), the ratio of constituent units TiO_2 and SiO_2 present in the catalyst can be specified by the molar ratio. Therefore, x means the molar ratio of TiO_2 present in the titanosilicate and (1-x) means the molar ratio of SiO_2 also present therein. In the other words, $x/(1-x)$ merely shows the molar ratio of titanium/silicon and does not exclude the presence of other elements in the crystalline MWW-type titanosilicate for the production of an oxidized compound.

[0027]

In composition formula (1), the range of x is from 0.0001 to 0.2, preferably from 0.005 to 0.2, more preferably from 0.01 to 0.1. In addition to the titanium introduced into the skeleton by substituting to silicon, a titanium species may be present at a site outside the crystal skeleton, for example, a 6-coordination titanium

species or an anatase-like titanium oxide may be present together, however, such a titanium species outside the skeleton promotes a side reaction or narrows the pores to inhibit the diffusion of a reaction substance and therefore, is preferably present in a smaller amount.

[0028]

The x specified in composition formula (1) shows an estimated ratio of titanium contained within the skeleton. In practice, when titanium is present outside the skeleton in addition to titanium within the skeleton, it is difficult to precisely quantitate titanium contained within the skeleton. In general, for example, on an ultraviolet visible absorption spectrum, the absorption in the vicinity of 210 nm is assigned to titanium within the skeleton, the absorption in the vicinity of 260 nm is assigned to a 6-coordination titanium species outside the lattice, and the absorption in the vicinity of 330 nm is assigned to an anatase-like titanium species. Therefore, if absorption is present in the vicinity of 210 nm, this reveals that the titanosilicate contains titanium within the skeleton. Actually, the titanosilicate catalyst of the present invention (I) has absorption in the vicinity of 220 nm and this reveals the presence of titanium within the skeleton. However, when absorption is present at other wavelengths, it is difficult to quantitatively discuss the ratio of

these titanium species present even by combining other means such as nuclear magnetic resonance method or infrared absorption method.

[0029]

Only one clearly known fact is that the value of the molar ratio of titanium to silicon calculated from the ratio between titanium and silicon determined by the component analysis such as elemental analysis, is the maximum value of the amount of titanium contained within the skeleton. As described above, the molar ratio of titanium contained within the skeleton is difficult to directly determine and therefore, in the present invention, the molar ratio of titanium to silicon calculated by the component analysis as x in composition formula (1) is for convenience used as the molar ratio of titanium contained within the skeleton.

[0030]

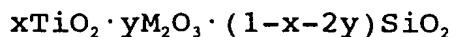
The crystalline titanosilicate catalyst of the present invention (I) having a structural code MWW of allowing titanium to substitute to silicon may contain an element other than titanium, silicon and oxygen, as long as it does not greatly cause adverse effect on the reactivity of the catalyst. In the case where the catalyst of the present invention (I) is produced by a production process using boron as a structure supporting agent, which is described

later, a slight amount of boron remains in many cases even if an operation for removing boron is performed. However, boron in a small amount does not have any great effect on the reactivity and therefore, may be substantially present. In principle, other trivalent metals such as aluminum, gallium, iron and chromium may also be used as a structure supporting agent in place of boron and in such a case, these elements may sometimes remain within and outside the skeleton.

[0031]

This case is the crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound of the present invention (II). That is, the present invention (II) is a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound, which is a catalyst for use in producing an oxidized compound by an oxidation reaction of a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or more other functional group using a peroxide as an oxidizing agent, wherein the catalyst has an MWW structure and is represented by the following composition formula (2):

Composition formula (2)



(wherein M represents at least one element selected from the group consisting of aluminum, boron, chromium, gallium

and iron, x is a number of 0.0001 to 0.2 and y is a number of 0.0001 to 0.1).

[0032]

In composition formula (2), x has the same the meaning as in composition formula (1) and y is also a molar ratio of constituent unit M_2O_3 present in the catalyst. Similarly to composition formula (1), $x/(1-x-2y)$ represents merely a molar ratio of "titanium"/"silicon" and $y/(1-x-2y)$ represents merely a ratio of "at least one element in total selected from the group consisting of aluminum, boron, chromium, gallium and iron"/"silicon" but these do not exclude the presence of other elements in the catalyst of the present invention (II). In composition formula (2), y is a number of 0.0001 to 0.1, preferably 0.05 or less, more preferably 0.03 or less.

[0033]

In composition formula (2) of the present invention (II), y can be determined from the component analysis values similarly to x in composition formula (1) of the present invention (I). The presence form thereof may be either within the skeleton or outside the skeleton. M is at least one element selected from the group consisting of aluminum, chromium, gallium and iron, and has a valence number of 3.

[0034]

As used in the synthesis of MCM-22, an alkali metal such as sodium and potassium can be generally expected to work as a mineralizing agent and therefore, may be used in the production of the catalyst of the present invention (I) or (II) for the purpose of accelerating the crystallization. However, in general, the alkali metal has a possibility of inhibiting the catalytic function of the crystalline titanasilicate and therefore, is preferably removed by ion exchange or the like.

[0035]

The MWW structure, which is one of known structures of the molecular sieve, is greatly characterized by having a pore comprising an oxygen 10-membered ring and by having a super cage ($0.7 \times 0.7 \times 1.8$ nm). The structure has been approved by IZA after the publication of Atlas. The details of the structure can be inspected, for example, on the homepage (<http://www.iza-structure.org/>) of the IZA Structure Commission (as of September, 2000). Examples of known molecular sieves having this structure include MCM-22 (Science, Vol. 264, 1910 (1994)), SSZ-25 (European Patent No. 231860), ITQ-1 (Chem. Mater., Vol. 8, 2415 (1996) and J. Phys. Chem. B, Vol. 102, 44 (1998)), ERB-1 (European Patent No. 203032) and PSH-3 (U.S. Patent 449409). The molecular sieve having structural code MWW can be identified by the

pattern of its characteristic X-ray diffraction (hereinafter simply referred to as "XRD"). The XRD pattern may also be available as a simulation pattern of ITQ-1, for example, on the above-described homepage. Representative examples of the diffraction line include those shown in Table 1 below.

[0036]

[Table 1]

Table 1 Diffraction Line Given by MWW Structure

d/Å±0.1	Relative Strength (s: strong, m: moderate, w: weak)
12.3±0.6	s
11.0±0.6	s
8.8±0.5	s
6.2±0.4	m
5.5±0.3	w
3.9±0.2	m
3.7±0.2	w
3.4±0.2	s

[0037]

The present invention (III) is described below. The present invention (III) is a process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound, comprising the following first and second steps:

First step:

a step of heating a mixture containing a template compound, a titanium-containing compound, a boron-containing compound, a silicon-containing compound and water to obtain a precursor;

Second step:

a step of calcining the precursor obtained in the first step to obtain a crystalline titanosilicate.

[0038]

The crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound of the present invention can also be synthesized by the conventionally known direct synthesis method or the post-synthesis method such as atom-in-plantation. In the case of atom-in-plantation, the catalyst may be synthesized, for example, by preparing a molecular sieve having a MWW structure containing boron or aluminum, removing at least a part of boron or aluminum through a water vapor treatment or the like and then contacting the residue with a titanium compound such as titanium trichloride.

[0039]

The more efficient production process includes the production process of the present invention (III). That is, the process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized

compound of the present invention (III) is a production process of a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound, characterized by comprising two steps in the process of producing the catalyst, i.e., a step of heating a mixture containing a template compound, a titanium-containing compound, a boron-containing compound, a silicon-containing compound and water to obtain a precursor and a step of calcining the obtained precursor to obtain a crystalline MWW-type titanosilicate for the production of an oxidized compound.

[0040]

The first step is described below. The first step in the process for producing the crystalline titanosilicate of the present invention (III) is a step of heating a mixture containing a template compound, a titanium-containing compound, a boron-containing compound, a silicon-containing compound and water to obtain a precursor.

[0041]

The "template compound" as used herein is a compound having a function of, in the synthesis of zeolite having MWW structure, determining the structure thereof, particularly, the shape of pore and this compound is not particularly limited as long as it can be removed later by calcining. Examples thereof generally include nitrogen-containing compounds. Specific examples thereof include

piperidine, hexamethyleneimine and/or a mixture thereof, however, the present invention is not limited thereto.

[0042]

The titanium-containing compound which can be used in the first step is not particularly limited as long as the compound can produce gel. Specific examples of the titanium-containing compound include titanium oxide, titanium halide and tetraalkylorthotitanates, however, the present invention is not limited thereto. Among these, in view of easy handleability, titanium halide and tetraalkylorthotitanates are preferred. Specifically, titanium tetrafluoride, tetraethylorthotitanate, tetrapropylorthotitanate and tetrabutylorthotitanate are suitably used.

[0043]

The boron-containing compound which can be in the first step is not particularly limited. Preferred specific examples thereof include boronic acid, and this may also be used in the form of a boronate such as sodium boronate.

[0044]

The silicon-containing compound which can be used in the first step is not particularly limited and specific examples thereof include silicic acid, silicate, silicon oxide, silicon halide, fumed silicas, tetraalkylorthosilicates and colloidal silica. In any of these, the purity

is preferably high but particularly, colloidal silica preferably has a smaller alkali content.

[0045]

The ratio of titanium and silicon in the mixture of the first step is in terms of the molar ratio preferably 0.001 to 0.3 : 1 (titanium : silicon), more preferably 0.005 to 0.2 : 1 (titanium : silicon), still more preferably 0.01 to 0.2:1 (titanium : silicon).

[0046]

The ratio of boron and silicon in the mixture of the first step is in terms of the molar ratio preferably 0.3 to 10 : 1 (boron : silicon), more preferably 0.5 to 5 : 1 (boron : silicon), still more preferably 1 to 2 : 1 (boron : silicon).

[0047]

The ratio of water and silicon in the mixture of the first step is in terms of the molar ratio preferably 5 to 200 : 1 (water : silicon), more preferably 15 to 50 : 1 (water : silicon).

[0048]

The ratio of the template compound and silicon in the mixture of the first step is in terms of the molar ratio preferably 0.1 to 5:1 (template compound : silicon), more preferably 0.3 to 3 : 1 (template compound : silicon), still more preferably 0.5 to 2 : 1 (template compound :

silicon).

[0049]

These ratios of the mixture in the first step are not particularly limited but each is preferably in the above-described range so as to efficiently obtain a high-activity crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound. An element other than those elements may be present together in the mixture of the first step, however, the amount of an alkali metal or an alkaline earth metal is preferably smaller because if an alkali metal or an alkaline earth metal is present in a large amount, titanium may be prevented from entering into the skeleton. To speak specifically, for example, the total molar number of an alkali metal or an alkaline earth metal is preferably smaller than the molar number of titanium.

[0050]

The heating temperature in the first step is not particularly limited. However, in the case of synthesizing a precursor, the heating is preferably performed under hydrothermal reaction conditions. The term "hydrothermal reaction" as used herein means, as described in Hyojun Kagaku Yogo Jiten (Standard Chemical Glossary), Item "Hydrothermal Reaction", Japan Chemical Association (compiler), Maruzen (March 30, 1991), a synthesis or a modification reaction of a substance performed in the

presence of water at high temperature, particularly water at high temperature and high pressure, and a synthesis reaction utilizing the hydrothermal reaction is called "hydrothermal synthesis". Therefore, in the first step, the heating is preferably performed under hydrothermal synthesis conditions such that a mixture containing a template compound, a titanium-containing compound, a boron-containing compound, a silicon-containing compound and water is charged into a closed container such as autoclave and pressurized while heating. The heating temperature is preferably from 110 to 200°C, more preferably from 120 to 190°C.

[0051]

If the temperature in the hydrothermal synthesis is less than this range, the objective product may not be obtained or even if obtained, the heating may take a long period of time and this is not practical, whereas if the temperature exceeds this range, the yield of the objective product in an oxidation reaction using the finally obtained catalyst disadvantageously decreases.

[0052]

The hydrothermal synthesis is usually performed for 2 hours to 30 days, preferably for 3 hours to 10 days. If the hydrothermal synthesis time is less than this range, crystallization insufficiently proceeds and a high-

performance catalyst may not be obtained. On the other hand, even if the hydrothermal synthesis is performed for a time period in excess of this range, the catalytic activity is not substantially enhanced but rather adverse effects may disadvantageously occur, such as conversion into another phase or increase in the particle size.

[0053]

The second step is described below. The second step is a step of calcining the precursor obtained in the first step to obtain a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound.

[0054]

The method of calcining the precursor is not particularly limited and may be performed under known conditions in usual catalyst calcination. The calcination may be performed in the closed system or in the flow system and if desired, may be performed in an inert gas stream, such as nitrogen. The calcination temperature is preferably from 200 to 700°C, more preferably from 300 to 650°C, most preferably from 400 to 600°C. If the calcination temperature is less than 200°C, the template compound may not be satisfactorily removed, whereas if it exceeds 700°C, destruction of the MWW-type crystal structure may occur and in turn, this adversely affects the catalytic performance.

[0055]

The process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound of the present invention (III) is described in detail below. The process for producing a catalyst of the present invention (III) is a process of converting a titanosilicate in the amorphous state using piperidine or hexamethyleneimine as a template and using boron (boric acid) as a structure supporting agent, into a precursor having a lamella phase called MCM-22(P) (first step) and then calcining the precursor (second step) to obtain a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound.

[0056]

Describing more specifically the process for producing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound, for example, an aqueous solution of piperidine or hexamethyleneimine (template) is divided into two portions, tetraalkylorthotitanate is added to and dissolved in one portion, a boron compound is added to and dissolved in another portion, and silica is further added to each portion, followed by stirring, to prepare two kinds of homogenous gels containing titanium or boron.

[0057]

After these two kinds of gels are thoroughly mixed and

stirred, the mixture is transferred to a closed container such as autoclave and subjected to a hydrothermal synthesis. The obtained solid product is separated from the mother liquor by filtration or the like, thoroughly washed with water and then dried. By calcining the thus-obtained precursor, a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound can be obtained.

[0058]

The catalyst which can be obtained by the production process of the present invention (III) may be used as a catalyst for an oxidation reaction as it is, but boron introduced inside or outside the skeleton present in the titanosilicate obtained by this production process or the anatase phase resultant from the condensation of titanium itself which does not participate in an oxidation reaction may be at least partially removed by contacting the catalyst with an acid. By this contact with an acid, the obtained crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound can have higher performance.

[0059]

An effect may be brought out by performing this contact with an acid before or after calcination or both before and after calcination in the process of producing a crystalline MWW-type titanosilicate catalyst for the

production of an oxidized compound, however, a highest effect can be obtained by contacting the catalyst in the precursor state before calcination and in this case, the by-product anatase phase due to calcination can be greatly suppressed.

[0060]

The "contact with an acid" as used herein specifically means that a solution containing an acid or an acid itself is contacted with the precursor obtained after the first step or the titanosilicate obtained after the second step. The contacting method is not particularly limited and may be a method of spraying or coating an acid or an acid solution to the precursor or titanosilicate or a method of dipping the precursor or titanosilicate in an acid or an acid solution. The method of dipping the precursor or titanosilicate in an acid or an acid solution is simple and easy and this method is preferred.

[0061]

The acid used for the contact with an acid may be an inorganic acid, an organic acid or a salt thereof. Specific examples of preferred inorganic acids include hydrochloric acid, sulfuric acid, nitric acid and phosphoric acid. Specific examples of preferred organic acids include formic acid, acetic acid, propionic acid and tartaric acid. Examples of the salt thereof include sodium salt, potassium

salt, calcium salt, magnesium salt and ammonium salt.

[0062]

The contact with an acid may be performed either before or after calcination as described above but is preferably performed before the calcination so as to attain a higher effect. A solid substance such as precursor is dipped in an acid solution in an amount of approximately from 5 to 100 ml per g of the solid substance and kept for a predetermined time and thereafter, the solid is recovered by filtration or the like and then thoroughly washed with a solvent. Stirring is not always necessary but may be performed.

[0063]

In the case of using the acid in the form of a solution, the solvent is not particularly limited. Specific examples thereof include water, alcohols, ethers, esters and ketones, and among these, water is more suitable.

[0064]

The acid concentration is not particularly limited but is suitably on the order of 0.1 to 10 mol/l. The temperature may be from 0 to 200°C but is preferably from 50 to 180°C, more preferably from 60 to 150°C. The treatment time may be from 0.1 hours to 3 day but is suitably from 2 hours to 1 day.

[0065]

The present invention (IV) is described below. The present invention (IV) is a process for producing an oxidized compound comprising performing an oxidation reaction of a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or more other functional group using a peroxide as an oxidizing agent in the presence of the crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound of the present invention (I) or (II). According to the production process of an oxidized compound of the present invention (IV), only the oxidation reaction of a carbon-carbon double bond can be selectively performed without affecting other functional groups of the compound having a carbon-carbon double bond and one or more other functional group. Needless to say, other functional groups may be simultaneously reacted to obtain an entirely different objective substance and such a case is of course included in the present invention (IV).

[0066]

Specific examples of the peroxide which can be used in the present invention (IV) include hydrogen peroxide and organic peroxides. Examples of the organic peroxide include tert-butyl hydroperoxide, tert-aminohydroperoxide, cumene hydroperoxide, ethylbenzene hydroperoxide, cyclohexyl

hydroperoxide, methylcyclohexyl hydroperoxide, tetraphosphoric hydroperoxide, isobutylbenzene hydroperoxide, ethylnaphthalene hydroperoxide and peracetic acid, however the present invention is not limited thereto. These peroxides may be used in combination of two or more thereof.

[0067]

The peroxide used is most preferably hydrogen peroxide and an aqueous hydrogen peroxide solution having a concentration of 30 wt%, 60 wt%, 90 wt% or the like may be used. The amount of peroxide added is not particularly limited and may be equivalent or more to the carbon-carbon double bond of the compound having a carbon-carbon double bond and one or more other functional group, which is a raw material subjected to an oxidation reaction, or may be equivalent or less depending on the conditions.

[0068]

The compound having a carbon-carbon double bond and one or more other functional group for use in the process for producing an oxidized compound of the present invention (IV) is not particularly limited and may be any compound as long as it has a carbon-carbon double bond and one or more other functional group within one molecule. In this case, a carbon-carbon double bond is of course included in the "other functional group".

[0069]

Specific examples of the other functional group include an alkenyl group, an alkynyl group, an aryl group, an arene group, an alcohol group, a phenol group, an ether group, an epoxide group, a halogen group, an aldehyde group, a ketone group, a carbonyl group, an ester group, an amide group, a cyanate group, an isocyanate group, a thiocyanate group, an amine group, a diazo group, a nitro group, a nitrile group, a nitroso group, a sulfide group, a sulfoxide group, a sulfone group, a thiol group, an orthoester group, a urea group and imine group, however, the present invention is not limited thereto. Two or more of the same functional group may be contained or two or more kinds of functional groups may be contained.

[0070]

More specific examples of the compound having a carbon-carbon double bond and one or more other functional group include allyl ethers, compounds having from 3 to 10 carbon atoms, ethers of polyhydric alcohol, and carboxylic acid esters. Of course, these compounds may be used in combination of two or more thereof.

[0071]

More specifically, examples of the allyl ethers include allyl methyl ether, allyl ethyl ether, allyl propyl ether, allyl butyl ether, allyl vinyl ether and diallyl

ether.

Examples of the compounds having from 3 to 10 carbon atoms include allyl alcohol, allyl bromide, allyl chloride acrolein, methacrolein and acrylic acid.

[0072]

Examples of the ethers of polyhydric alcohol include ethylene glycol monoalkenyl ether, ethylene glycol dialkenyl ether, 1,2-propanediol monoalkenyl ether, 1,2-propanediol dialkenyl ether, 1,3-propanediol monoalkenyl ether, 1,3-propanediol dialkenyl ether, 1,2-butanediol monoalkenyl ether, 1,2-butanediol dialkenyl ether, 1,3-butanediol monoalkenyl ether, 1,3-butanediol dialkenyl ether, 1,4-butanediol monoalkenyl ether, 1,4-butanediol dialkenyl ether and pentaerythritol monoalkenyl ether, pentaerythritol dialkenyl ether, pentaerythritol trialkenyl ether and pentaerythritol tetraalkenyl ether.

[0073]

Examples of the carboxylates include allyl formate, allyl acetate, allyl tartrate, allyl propionate and allyl methacrylate.

[0074]

Examples of the most preferred combination include a combination such that the compound having a carbon-carbon double bond and one or more other functional group is diallyl ether, allyl acetate, allyl methacrylate or allyl

alcohol and the oxidizing agent is hydrogen peroxide.

[0075]

The amount of the crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound used in the process for producing an oxidized compound of the present invention (IV) is not particularly limited. The preferred range thereof varies depending on the kind of oxidation reaction, the reaction temperature, the reactivity and temperature of substrate, the concentration of peroxide, the kind and concentration of solvent, and the reaction form (batch system, continuous system). In the case of use in a slurry system, the amount of the catalyst is usually in terms of the concentration in the reactant mixture in the range suitably from 0.1 to 20 wt%, more preferably from 0.5 to 10 wt%. In the case of fixed bed flow reaction system, the apparent catalytic amount is preferably larger than the above-described range.

[0076]

The shape of the crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound is not particularly limited. The shape may be powder, micro-ball, pellet or extrusion molded article or the catalyst may also be supported on a support. In molding the catalyst, a binder may be used. The binder or support is preferably a substance which is substantially non-acidic or weakly

acidic and which does not accelerate the decomposition reaction of the peroxide or the decomposition reaction of the objective oxidized compound.

[0077]

The oxidation reaction in the process for producing an oxidized compound of the present invention (IV) may be performed without using a solvent or in the presence of an appropriate solvent. Examples of the appropriate solvent include alcohols, ketones, nitriles and water. Specific examples of alcohols include methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, tert-butanol, amyl alcohol, ethylene glycol, propylene glycol and 1,2-butanediol. Specific examples of ketones include acetone, methyl ethyl ketone and diethyl ketone. Specific examples of nitriles include acetonitrile, propionitrile and benzonitrile. These may be used independently or as a mixture thereof. Among these solvents, preferred are acetone, acetonitrile and water, and more preferred is acetonitrile.

[0078]

In the process for producing an oxidized compound of the present invention (IV), the reaction temperature at the oxidation reaction, which is not particularly limited, is preferably from 0 to 150°C, more preferably from 10 to 100°C. If the temperature is less than 0°C, the reaction rate is

low and this is not practical, whereas if the temperature exceeds 150°C, the decomposition reaction of peroxide seriously proceeds and furthermore, the decomposition reaction of the objective product is disadvantageously accelerated.

[0079]

The oxidation reaction is generally an exothermic reaction and therefore, the heat of reaction is preferably removed by a suitable method so as to control the reaction temperature to a constant range. The reaction pressure is not particularly limited.

[0080]

The oxidation reaction in the process for producing an oxidized compound of the present invention (IV) may be performed by any method in a batch system, a continuous system or a semi-continuous system using a suitable reactor or reaction apparatus such as fixed bed, transportation bed, stirring slurry or CSTR reactor. The mixture containing a crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound, a compound having a carbon-carbon double bond and one or more other functional group and a peroxide may be mixed all at once or may be mixed in sequence.

[0081]

In this reaction, the objective oxidized compound may

be separated by a separating purification method in the normal purification process. More specifically, for example, when the reaction is performed in a batch system, the oxidized compound, of which production reaches the desired region, may be separated and recovered from the reaction mixture using any known method such as fractional distillation, extract distillation or liquid-liquid extraction.

[0082]

In the case of a slurry-type reactor, the crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound can be recovered by a suitable method such as filtration or centrifugation, and the recovered catalyst can be reused as a catalyst for oxidation reaction.

[0083]

In the case of a fixed bed-type reactor, the crystalline MWW-type titanosilicate catalyst for the production of an oxidized compound can be easily separated from the product oxidized compound, the solvent, the unreacted compound having a carbon-carbon double bond and one or more other functional group and the peroxide, while keeping the catalyst in the reactor.

[0084]

In the process for producing an oxidized compound of the present invention (IV), the recovered crystalline MWW-

type titanasilicate catalyst for the production of an oxidized compound, the unreacted compound having a carbon-carbon double bond and one or more other functional group and the peroxide can be reused after purification by an appropriate method or without passing through purification.

[0085]

In the present invention (IV), the recovered crystalline MWW-type titanasilicate catalyst for the production of an oxidized compound generally decreases in the activity every each repeated use and may fail in exhibiting its initial activity. In such a case, the recovered catalyst must be regenerated. The regeneration of the recovered catalyst may be performed by a conventionally known method and to speak specifically, the catalyst may be regenerated to the initial activity, for example, by calcining the catalyst in air at a temperature of 100 to 600°C.

[0086]

[Examples]

The present invention is described in greater detail below by referring to the Examples, however, these Examples are set forth only to show the outline of the present invention and the present invention should not be construed as being limited thereto.

[0087]

[Description of Terms in Examples and Comparative Examples]

Calculation Method of Conversion of Allyl Alcohol:

The molar ratio of allyl alcohol consumed in the reaction based on the allyl alcohol charged prior to the reaction. The allyl alcohol consumed in the reaction was calculated from the increase and decrease of allyl alcohol between before and after the reaction.

Calculation Method of Selectivity of Glycidol:

The molar ratio of glycidol and glycerin calculated from the analysis results of filtrate after the reaction.

Calculation Method of Conversion of Hydrogen Peroxide:

The ratio of hydrogen peroxide consumed in the reaction based on the hydrogen peroxide charged prior to the reaction. The hydrogen peroxide consumed in the reaction was calculated from the increase and decrease of hydrogen peroxide between before and after reaction.

[0088]

Calculation of Effective Ratio of Hydrogen Peroxide:

The effective ratio of hydrogen peroxide indicates a ratio of hydrogen peroxide exclusive of hydrogen peroxide consumed in the decomposition into oxygen out of hydrogen peroxide consumed in the reaction, namely, a ratio of hydrogen peroxide consumed in the epoxidization reaction out of the consumed hydrogen peroxide.

Yield of Epoxide:

The yield of the objective oxidized product epoxide compound based on hydrogen peroxide after the completion of the oxidation reaction using hydrogen peroxide. This indicates a molar ratio of the amount of epoxide compound produced to the amount of hydrogen peroxide charged.

Reduction Ratio of Catalytic Activity:

This indicates a decrement in the molar amount of the epoxide compound produced by repeatedly using the catalyst based on the molar amount of the epoxide compound produced using an unused catalyst.

[0089]

[Apparatuses for Analysis in Examples and Comparative Examples]

Analysis Method of Titanosilicate Element:

A titanosilicate was weighed and charged into a Teflon beaker, hydrofluoric acid (50% by mass) was added thereto and dissolved, pure water was added thereto and the obtained solution was subjected to a component analysis for titanium, silicon and boron using a desktop-type plasma emission analysis apparatus (SPS 1700, manufactured by Seiko Denshi Kogyo K.K.).

[0090]

Analysis of Concentration of Organic Compound in Filtrate of Reaction Mixture:

The concentration was measured using the following gas chromatography analysis apparatus and analysis conditions.

In the analysis, an internal standard method was used. More specifically, 1 ml of 1,4-dioxane as an internal standard was added to 10 ml of a reaction solution to prepare an analysis solution and 0.4 μ l of the analysis solution was injected.

Gas chromatography:

GC-14B manufactured by Shimadzu Seisakusho

Column: capillary column TC-WAX (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 μ m)

Carrier gas: nitrogen (split ratio: 20, column flow rate: 2 ml/min)

Temperature condition:

The temperatures of detector and vaporization room were 200°C and the column temperature was kept at 50°C for 5 minutes from the initiation of analysis, then elevated to 150°C at a temperature-rising rate of 10°C/min, kept at 150°C for 10 minutes, thereafter elevated to 200°C at a temperature-rising rate of 10°C/min and kept for 25 minutes.

Detector: FID (H_2 pressure: 70 kPa, air pressure: 100 kPa)

[0091]

Analysis of Concentration of Hydrogen Peroxide in Filtrate of Reaction Mixture

A potential difference titration was performed using an automatic potential difference titration apparatus AT-012 manufactured by Kyoto Denshi Kagaku Kogyosha and using a solution containing Ce(IV) as a titration reagent.

[0092]

Example 1: production of Catalyst 1

182.5 g of piperidine (purity: 98%, produced by Wako Pure Chemical Industries, Ltd.) (hereinafter simply referred to as "PI") was dissolved in 513 g of ion exchanged water at 25°C to prepare an aqueous piperidine solution. This aqueous piperidine solution was divided into two equal parts. While vigorously stirring, 18.0 g of tetrabutylorthotitanate (purity: 95%, produced by Wako Pure Chemical Industries, Ltd.) was added to one part and 124.2 g of boric acid (purity: 99.5%, produced by Wako Pure Chemical Industries, Ltd.) was added to another part. After stirring for 30 minutes to allow the hydrolysis reaction of tetrabutylorthotitanate to completely proceed, 45 g of fumed silica (Cab-o-sil M7D) was added to each solution containing titanium or boron. After the addition of silica, the solutions were stirred for 1 hour to obtain two kinds of homogenous gels. These two kinds of gels were mixed and

the mixed gel was continuously stirred for 1 hour and 30 minutes to obtain a mixture having a molar ratio of $1 \cdot \text{SiO}_2 : 0.033 \cdot \text{TiO}_2 : 0.67 \cdot \text{B}_2\text{O}_3 : 1.4 \cdot \text{PI} : 19 \cdot \text{H}_2\text{O}$.

[0093]

This gel was transferred to a 2-liter Teflon-made autoclave, stirred at a temperature of 130°C and a revolution number of 100 rpm for 24 hours, subsequently stirred at a temperature of 150°C and a revolution number of 100 rpm for 24 hours, and further stirred at a temperature of 170°C and a revolution number of 100 rpm for 120 hours. After the completion of stirring, the content was cooled to 25°C, a solid product was separated from the content by filtration, and the solid product was washed using ion exchanged water. The washing was repeated until the pH of washing water became 9 or less. The thus-obtained solid product was dried at a temperature of 50°C and thereto, 20 ml of 6 mol/l nitric acid was added per 1 g of the obtained solid product to perform an acid treatment at a temperature of 100°C for 20 hours. After the completion of the acid treatment, the solid was collected by filtration and calcined at a temperature of 530°C for 10 hours to obtain final objective product MWW-type titanosilicate Catalyst 1.

The molar ratio of titanium/silicon and the molar ratio of boron/silicon of Catalyst 1 were measured. The

results are shown in Table 2.

[0094]

Example 2: production of Catalyst 2

MWW-type titanosilicate Catalyst 2 was obtained in the same manner as in Example 1 except for using 1.0 mol/l of sulfuric acid in place of 6 mol/l of nitric acid in the acid treatment.

The molar ratio of titanium/silicon and the molar ratio of boron/silicon of Catalyst 2 were measured. The results are shown in Table 2.

Example 3: production of Catalyst 3

MWW-type titanosilicate Catalyst 3 was obtained in the same manner as in Example 1 except for using 2.0 mol/l of sulfuric acid in place of 6 mol/l of nitric acid in the acid treatment.

The molar ratio of titanium/silicon and the molar ratio of boron/silicon in Catalyst 3 were measured. The results obtained are shown in Table 2.

Example 4: production of Catalyst 4

182.5 g of PI (purity: 98%, produced by Wako Pure Chemical Industries, Ltd.) was dissolved in 513 g of ion exchanged water at 25°C to prepare an aqueous piperidine solution. This aqueous piperidine water was divided into two equal parts. While vigorously stirring, 18.0 g of tetrabutylorthotitanate (purity: 95%, produced by Wako Pure

Chemical Industries, Ltd.) was added to one part and 124.2 g of boric acid (purity: 99.5%, produced by Wako Pure Chemical Industries, Ltd.) was added to another part. After stirring for 30 minutes to allow the hydrolysis reaction of tetrabutylorthotitanate to completely proceed, 45 g of fumed silica (Cab-o-sil M7D) was added to each solution containing titanium or boron. After the addition of silica, the solutions were stirred for 1 hour to obtain two kinds of homogenous gels. These two gels were mixed and the mixed gel was continuously stirred for 1 hour and 30 minutes to obtain a mixture having a molar ratio of $1 \cdot \text{SiO}_2 : 0.033 \cdot \text{TiO}_2 : 0.67 \cdot \text{B}_2\text{O}_3 : 1.4 \cdot \text{PI} : 19 \cdot \text{H}_2\text{O}$.

[0095]

This gel was transferred to a 2-liter Teflon-made autoclave, stirred at a temperature of 130°C and a revolution number of 100 rpm for 24 hours, subsequently stirred at a temperature of 150°C and a revolution number of 100 rpm for 24 hours, and further stirred at a temperature of 170°C and a revolution number of 100 rpm for 120 hours. After the completion of stirring, the content was cooled to 25°C, a solid product was separated from the content by filtration, and the solid product was washed using ion exchanged water. The washing was repeated until the pH of washing water became 9 or less. The thus-obtained solid product was calcined at a temperature of 530°C for 10 hours

to obtain final objective product MWW-type titanosilicate Catalyst 4.

The molar ratio of titanium/silicon and the molar ratio of boron/silicon of Catalyst 4 were measured. The results are shown in Table 2.

[0096]

Example 5: production of Catalyst 5

182.5 g of PI (purity: 98%, produced by Wako Pure Chemical Industries, Ltd.) was dissolved in 513 g of ion exchanged water at 25°C to prepare an aqueous piperidine solution. This aqueous piperidine water was divided into two equal parts. While vigorously stirring, 18.0 g of tetrabutylorthotitanate (purity: 95%, produced by Wako Pure Chemical Industries, Ltd.) was added to one part and 124.2 g of boric acid (purity: 99.5%, produced by Wako Pure Chemical Industries, Ltd.) was added to another part. After stirring for 30 minutes to allow the hydrolysis reaction of tetrabutylorthotitanate to completely proceed, 45 g of fumed silica (Cab-o-sil M7D) was added to each solution containing titanium or boron. After the addition of silica, the solutions were stirred for 1 hour to obtain two kinds of homogenous gels. These two gels were mixed and the mixed gel was continuously stirred for 1 hour and 30 minutes to obtain a mixture having a molar ratio of $1 \cdot \text{SiO}_2 : 0.033 \cdot \text{TiO}_2 : 0.67 \cdot \text{B}_2\text{O}_3 : 1.4 \cdot \text{PI} : 19 \cdot \text{H}_2\text{O}$.

[0097]

This gel was transferred to 2-liter Teflon-made autoclave, stirred at a temperature of 130°C and a revolution number of 100 rpm for 24 hours, then stirred at a temperature of 150°C and a revolution number of 100 rpm for 24 hours, further stirred at a temperature of 170°C and a revolution number of 100 rpm for 120 hours. After the completion of stirring, the content was cooled to 25°C, a solid product was separated from the content by filtration, and the solid product was washed using ion exchanged water. The washing was repeated until the pH of washing water became 9 or less. The thus-obtained solid product was dried at a temperature of 50°C and thereto, 20 ml of 6 mol/l nitric acid was added per 1 g of the obtained solid product to perform an acid treatment at a temperature of 100°C for 20 hours. After the completion of the acid treatment, the solid was collected by filtration and thereto, 20 ml of 2 mol/l nitric acid was further added per 1 g of the solid to perform an acid treatment at a temperature of 100°C for 20 hours. The thus-treated solid was calcined at a temperature of 530°C for 10 hours to obtain final objective product MWW-type titanosilicate Catalyst 5.

The molar ratio of titanium/silicon and the molar ratio of boron/silicon of Catalyst 5 were measured. The results are shown in Table 2.

[0098]

The molar ratio of titanium/silicon and the molar ratio of boron/silicon of Catalysts 1 to 5 obtained in Examples 1 to 5 are shown in Table 2.

[0099]

[Table 2]

	No.	Molar Ratio of Titanium/Silicon	Molar Ratio of Boron/Silicon
Example 1	Catalyst 1	0.0217	0.0204
Example 2	Catalyst 2	0.0132	0.0244
Example 3	Catalyst 3	0.0068	0.0294
Example 4	Catalyst 4	0.0323	0.0910
Example 5	Catalyst 5	0.0074	0.0016

[0100]

Example 6: production of oxidized compound using MWW-type titanosilicate Catalyst 1

To a 20 ml-volume three neck flask equipped with a thermometer, a reflux condenser and a magnetic stirrer, 0.58 g (10 mmol) of allyl alcohol and 3.9 g (5 ml) of acetonitrile were added and thereinto, MWW-type titanosilicate Catalyst 1 (70 mg) of Example 1 was charged. The flask was heated in a water bath at 60°C and the mixture was vigorously stirred. Immediately after the temperature of reaction mixture reacted 57°C, 1.1 g (10 mmol as hydrogen peroxide) of an aqueous 30 wt% hydrogen peroxide solution was added to the system and by taking this point as the

reaction initiation time, the stirring was continued until the passing of 30 minutes after the reaction initiation. After 30 minutes from the reaction initiation, the reaction mixture was immediately cooled with ice to stop the reaction. Thereafter, the reaction mixture was filtered to separate unreacted allyl alcohol, unreacted hydrogen peroxide, water, product and solvent from catalyst. At this time, the concentration of organic substances in the filtrate was analyzed by gas chromatography and the concentration of unreacted hydrogen peroxide was determined by potential difference titration using Ce(IV). The reaction results are shown in Table 3. The conversion of allyl alcohol was 87.0% and the selectivity of glycidol as the product epoxide compound was 99.9%. Furthermore, the conversion of hydrogen peroxide was 87.9% and the effective ratio of hydrogen peroxide was 99.0%.

[0101]

[Table 3]

	Kind of Catalyst			Solvent Used in Reaction	Conversion (%)		Selectivity (mol%) ^{*3}		Effective Ratio of Hydrogen Peroxide (%)
	No.	Molar Ratio of Titanium/ Silicon ^{*5}	Molar Ratio of Boron/ Silicon ^{*5}		Allyl Alcohol ^{*1}	Hydrogen Peroxide ^{*2}	Glycidol	Glycerin	
Example 6	Catalyst 1	0.0217	0.0204	Acetonitrile	87.0	87.9	99.9	0.1	99.0
Example 7	Catalyst 2	0.0132	0.0244	Acetonitrile	42.6	45.3	98.1	1.9	94.1
Example 8	Catalyst 3	0.0068	0.0294	Acetonitrile	16.2	17.2	92.1	7.9	94.2
Example 9	Catalyst 4	0.0323	0.0910	Acetonitrile	3.1	4.9	32.0	68.0	63.5
Example 10	Catalyst 5	0.0074	0.0016	Acetonitrile	12.4	13.4	94.5	5.5	92.3
Example 11	Catalyst 1	0.0217	0.0204	Water	82.3	97.6	99.9	0.1	84.3
Example 12	Catalyst 1	0.0217	0.0204	Ethanol	32.5	33.0	91.0	9.0	98.5
Comparative Example 1	MFI-type	0.0222	-	Acetonitrile	26.4	28.9	87.9	12.1	91.3

*1 Conversion of allyl alcohol: consumed allyl alcohol (mol)/raw material allyl alcohol (mol) × 100 (%)
 *2 conversion of hydrogen peroxide: consumed hydrogen peroxide (mol)/raw material hydrogen peroxide (mol) × 100 (%)

*3 Selectivity of glycidol: glycidol (mol)/[glycidol (mol) + glycerin (mol)] × 100 (mol%)

Selectivity of glycerin: glycerin (mol)/[glycidol (mol) + glycerin (mol)] × 100 (mol%)

*4 Effective ratio of hydrogen peroxide: [glycidol (mol) + glycerin (mol)]/consumed hydrogen peroxide (mol) × 100 (%)

*5 Molar ratio (calculated by ICP emission spectroscopic analysis)

[0102]

Example 7: production of oxidized compound using MWW-type titanasilicate Catalyst 2

The same operation as in Example 6 was performed except for using Catalyst 2 obtained in Example 2. The reaction results are shown in Table 3.

[0103]

Example 8: production of oxidized compound using MWW-type titanasilicate Catalyst 3

The same operation as in Example 6 was performed except for using Catalyst 3 obtained in Example 3. The reaction results are shown in Table 3.

[0104]

Example 9: production of oxidized compound using MWW-type titanasilicate Catalyst 4

The same operation as in Example 6 was performed except for using Catalyst 4 prepared in Example 4. The reaction results are shown in Table 3.

[0105]

Example 10: production of oxidized compound using MWW-type titanasilicate Catalyst 5

The same operation as in Example 6 was performed except for using Catalyst 5 prepared in Example 5. The reaction results are shown in Table 3.

[0106]

Example 11: examination of reaction solvent

The same operation as in Example 6 was performed except for adding 5 g (5 ml) of water as a solvent in place of using acetonitrile as a solvent. The reaction results are shown in Table 3.

[0107]

Example 12

The same operation as in Example 6 was performed except for adding 3.9 g (5 ml) of ethanol as a solvent in place of using acetonitrile as a solvent. The reaction results are shown in Table 3.

[0108]

Comparative Example 1: production of MFI-type titano-silicate catalyst and production of oxidized compound

To 500 ml-volume beaker equipped with a magnetic stirrer, 62.5 g of tetraethyl orthosilicate (produced by Wako Pure Chemical Industries, Ltd.) was added and subsequently, 107 g of an aqueous 20 mass% tetrapropyl ammonium hydroxide solution (produced by Tokyo Kasei Kogyo Co., Ltd.) was added at a temperature of 30°C over 10 minutes. After stirring for 1.0 hour, a mixture containing 38 g of isopropyl alcohol (produced by Wako Pure Chemical Industries, Ltd.) and 14 g of tetraorthotitanate (produced by Tokyo Kasei Kogyo Co., Ltd.) was added over 30 minutes.

After stirring at 30°C for 30 minutes, the mixture was heated using a water bath at 80°C and continuously stirred for 2 hours. To the obtained mixture, 230 g of water was added and the resulting solution was transferred to a Teflon-made autoclave and subjected to hydrothermal synthesis at 175°C for 48 hours. After the completion of hydrothermal synthesis, the content was taken out from the autoclave and centrifuged to separate the solid product. The thus-obtained solid product was washed with distilled water. After the completion of washing, the product was calcined at 500°C for 8 hours in the presence of air to remove organic substances. The product after the calcination was further washed for 12 hours using 20 ml of an aqueous 1.0 mol/l nitric acid solution per 1 g of the solid and after the completion of acid washing, the solid product was separated by filtration. Subsequently, this solid product was calcined at 500°C for 12 hours in the presence of air to obtain an objective MFI-type titanosilicate catalyst having a molar ratio of titanium/silicon of 0.0222.

The same operation as in Example 6 was performed except for using this MFI-type titanosilicate catalyst. The reaction results are shown in Table 3.

[0109]

Example 13: repeated use

To a 20 ml-volume three neck flask equipped with a thermometer, a reflux condenser and a magnetic stirrer, 0.23 g (4 mmol) of allyl alcohol and 7.9 g (10 ml) of acetonitrile were added and thereinto, MWW-type titanasilicate Catalyst 1 (100 mg) of Example 1 was charged. The resulting mixture was heated in a water bath at 60°C and vigorously stirred. Immediately after the temperature of the reaction mixture reached 57°C, 0.14 g (4 mmol as hydrogen peroxide) of 30 mass% hydrogen peroxide was added to the system and by taking this point as the reaction initiation time, the stirring was continued until the passing of 0.5 hours from the reaction initiation. After 0.5 hours from the reaction initiation, the reaction mixture was immediately cooled with ice to stop the reaction. Thereafter, the reaction mixture was filtered to separate unreacted allyl alcohol, unreacted hydrogen peroxide, water, product and solvent from catalyst. At this time, the concentration of obtained organic substances in the filtrate was analyzed by gas chromatography and the concentration of unreacted hydrogen peroxide was determined by potential difference titration using Ce(IV).

[0110]

After the catalyst recovered by filtration was dried,

a second time reaction was performed under the same conditions and after the completion of reaction, the mixture was filtered in the same manner as in the first time reaction to separate the filtrate from the catalyst. Then, the filtrate was analyzed and the catalyst was recovered.

Again, the catalyst recovered after the second time reaction was dried, a third time reaction was performed under the same conditions as in the first and second time reactions and after the completion of reaction, the mixture was separated and analyzed. In such a manner, the reaction was performed three times in total. The reaction results are shown in Table 4. The reduction ratio of activity, indicating the deterioration of catalyst, was 2% at the second time reaction and 10% at the third time reaction.

[0111]

[Table 4]

	Kind of Catalyst	Number of Use	Yield of Glycidol (%) ^{*1}	Reduction Ratio of Activity (%) ^{*3}
Example 13	Catalyst 1	1st time	88.3	0
		2nd time	86.7	2
		3rd time	79.5	10
Comparative Example 2	MFI-type ^{*2}	1st time	28.4	0
		2nd time	20.5	28
		3rd time	19.8	31

*1 Yield of glycidol: amount of glycidol produced (mol)/amount of raw material hydrogen peroxide (mol) × 100 (%)

- *2 MFI-type titanosilicate: molar ratio of titanium/silicon = 0.0222
- *3 Reduction ratio of activity: $[(\text{yield of glycidol at first time}) - (\text{yield of glycidol at second or third time})] / (\text{yield of glycidol at first time}) \times 100 (\%)$

[0112]

Comparative Example 2

The same operation as in Example 11 was performed except for using the MFI-structure titanosilicate catalyst having a molar ratio of titanium/silicon of 0.0222 obtained in Comparative Example 1. The reaction results are shown in Table 4. The reduction ratio of activity, indicating the deterioration of catalyst, was 28% at the second time reaction and 31% at the third time reaction.

[0113]

Example 14: examination of reaction substrate

To a 20 ml-volume three neck flask equipped with a thermometer, a reflux condenser and a magnetic stirrer, 0.98 g (10 mmol) of diallyl ether and 3.9 g (5 ml) of acetonitrile were added and thereinto, MWW-type titanosilicate Catalyst 1 (70 mg) of Example 1 was charged. The resulting mixture was heated in a water bath at 60°C and vigorously stirred. Immediately after the temperature of the reaction mixture reached 57°C, 1.1 g (10 mmol as hydrogen peroxide) of 30 mass% hydrogen peroxide was added to the system and by taking this point as the reaction initiation time, the stirring was continued until the

passing of 1 hour from the reaction initiation. After 1 hour from the reaction initiation, the reaction mixture was immediately cooled with ice to stop the reaction. Thereafter, the reaction mixture was filtered to separate unreacted diallyl ether, unreacted hydrogen peroxide, water, product and solvent from catalyst. At this time, the concentration of obtained organic substances in the filtrate was analyzed by gas chromatography and the concentration of unreacted hydrogen peroxide was determined by potential difference titration using Ce(IV). The reaction results are shown in Table 5. The yield of allyl glycidyl ether as an objective epoxide compound was 24.4%.

[0114]

[Table 5]

	Substrate	Epoxide Product	Yield of Epoxide (%) ^{*1}
Example 14	diallyl ether	allyl glycidyl ether	24.4
Example 15	allyl propyl ether	glycidyl propyl ether	42.6
Example 16	allyl chloride	epichlorohydrin	53.1
Example 17	styrene	styrene oxide	1.6
Comparative Example 3	diallyl ether	allyl glycidyl ether	16.7
Comparative Example 4	allyl propyl ether	glycidyl propyl ether	17.9
Comparative Example 5	allyl chloride	epichlorohydrin	20.1
Comparative Example 6	styrene	styrene oxide	1.1

*1 Yield of epoxide:

Amount of epoxide produced (mol)/amount of raw material
hydrogen peroxide (mol) × 100 (%)

[0115]

Example 15

The same operation as in Example 12 was performed except for using 1.00 g (10 mmol) of allyl propyl ether. The reaction results are shown in Table 5. The yield of glycidyl propyl ether as an objective epoxide compound was 42.6%.

[0116]

Example 16

The same operation as in Example 12 was performed except for using 0.77 g (10 mmol) of allyl chloride. The reaction results are shown in Table 5. The yield of epichlorohydrin as an objective epoxide compound was 53.1%.

[0117]

Example 17

The same operation as in Example 12 was performed except for using 1.04 g (10 mmol) of styrene. The reaction results are shown in Table 5. The yield of styrene oxide as an objective epoxide compound was 1.6%.

[0118]

Comparative Examples 3 to 6

The same operation as in Examples 14 to 17 was performed except for using the MFI structure titanosilicate

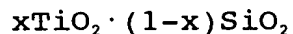
catalyst obtained in Comparative Example 1. The reaction results are shown in Table 5. The yield of allyl glycidyl ether was 16.7%, the yield of glycidyl propyl ether was 17.9%, the yield of epichlorohydrin was 20.1%, and the yield of styrene oxide was 1.1%, which were objective epoxide compounds.

[0119]

[Effects of the Invention]

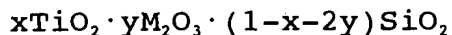
As described in the foregoing pages, it is apparent that as compared with conventionally known titanasilicate catalysts, the crystalline titanasilicate catalyst represented by the following composition formula (1) or (2) and having a structural code MWW described in the present specification works out to a very useful catalyst in the production of an oxidized compound from a compound having a carbon-carbon double bond and one or more other functional group by an oxidation reaction using a peroxide as an oxidizing agent:

Composition formula (1)



(wherein x is a number of 0.0001 to 0.2).

Composition formula (2)



(wherein M represents at least one element selected from the group consisting of aluminum, boron, chromium, gallium

and iron, x is a number of 0.0001 to 0.2 and y is a number of 0.0001 to 0.1).

[0120]

It is also apparent that according to the process for producing the above-described titanasilicate catalyst using hydrothermal synthesis described in the present specification, a high-performance crystalline MWW-type titanasilicate catalyst for the production of an oxidized compound can be obtained with good efficiency.

[NAME OF THE DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To provide a crystalline titanasilicate catalyst which can be used as a catalyst in the oxidation reaction of a compound having a carbon-carbon double bond and one or more other functional group, a process for producing the catalyst, and a process for producing an oxidized compound by an oxidation reaction using the catalyst.

[MEANS TO SOLVE THE PROBLEM]

It has been found that a crystalline titanasilicate having a structural code MWW effectively works as a catalyst in an oxidation reaction of a carbon-carbon double bond of a compound having a carbon-carbon double bond and one or more other functional group using a peroxide as an oxidizing agent, to highly selectively give the objective oxidized compound.

[SELECTED DRAWING] None